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In Situ Activation of Carbon Fiber Microdisk Electrodes

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Carbon Fiber microdisk electrodes (11 μm in diameter) were activated in situ via intense laser pulses produced by a small nitrogen laser. The laser beam was focussed down to a small spot size to ensure adequate power density. The laser treatment resulted in more Nernstian voltammtery for dopamine, 4-methylcatechol, and 3,4-dihydroxyphenylacetate in several different buffer systems over a range of pH. The effect of buffer composition and pH on the apparent electrode kinetics observed both before and after laser treatment was studied. An apparent cleaning of the electrode surface by the laser pulses results in more Nernstian voltammetry; however, voltammograms obtained in some buffer systems, particularly those containing citrate, show anomalous effects after laser treatment. A model of the activation process is presented which might explain the observed phenomenon by surface ablation exposing clean, active carbon, followed by adsorption of solution species. This activation procedure is presented as a simple, fairly inexpensive way to obtain consistent, repetitive voltammetry at carbon fiber microdisk electrodes.

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IN SITU LASER ACTIVATION OF CARBON FIBER MICRODISK ELECTRODES

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BRIEF

A small, pulsed nitrogen laser is used to activate carbon fiber microdisk electrodes. Cyclic voltammetry of dopamine, 4-methylcatechol, and 3,4-dihydroxyphenylacetate are compared before and after laser treatment, considering the effects of buffer content and pH.

ABSTRACT

Carbon Fiber microdisk electrodes (11 μm in diameter) were activated in situ via intense laser pulses produced by a small nitrogen laser. The laser beam was focussed down to a small spot size to ensure adequate power density. The laser treatment resulted in more Nernstian voltammetry for dopamine, 4-methylcatechol, and 3,4-dihydroxyphenylacetate in several different buffer systems over a range of pH. The effect of buffer composition and pH on the apparent electrode kinetics observed both before and after laser treatment was studied. An apparent cleaning of the electrode surface by the laser pulses results in more Nernstian voltammetry; however, voltammograms obtained in some buffer systems, particularly those containing citrate, show anomalous effects after laser treatment. A model of the activation process is presented which might explain the observed phenomenon by surface ablation exposing clean, active carbon, followed by adsorption of solution species. This activation procedure is presented as a simple, fairly inexpensive way to obtain consistent, repetitive voltammetry at carbon fiber microdisk electrodes.

INTRODUCTION

Due to íts inherent surface characteristics, carbon often exhibits poor electron transfer kinetics. This seems to be especially true for analysis of anionic species. Since the voltammetric response at carbon surfaces often degrade at an enhanced rate when placed in biological media, presumably due to adsorption of large molecules to the electrode surface, a process to renew the carbon surface before obtaining electrochemical information is sought.

Many investigators have studied the voltammetric response obtained at carbon electrodes following a variety of activation schemes (1-20). Glassy carbon (GC) (2-8) and highly ordered pyrolytic graphite (HOPG) (9-11) have been the carbon structures used for many of these investigations. These experiments have employed several activation schemes: electrochemical pretreatment (anodic) (2-4,10,16), thermal treatment (5,6), radio frequency plasma (8), and laser irradiation (9,16-20). More recently, primarily due to increased usage of microelectrodes, electrochemical activation of carbon fiber (12-14) and carbon ring (15) microelectrodes has been reported.

Several papers have appeared concerning laser activation of carbon electrodes of conventional size (17-20). This paper will apply an analogous technique using a small, inexpensive nitrogen laser to activate a carbon fiber microdisk electrode. Electromagnetic radiation of 337 nm from a pulsed laser source that is focussed onto the tip

of an 11 μm carbon fiber electrode appears to substantially increase the rate of heterogeneous electron transfer. In addition to being inexpensive, the methodology described here provides a means to easily, and repetitively obtain well-behaved voltammetry for catechols in situ. The overall goal of this research is to understand the activation process at carbon fiber electrodes.

EXPERIMENTAL SECTION

Chemicals. Working solutions of dopamine (DA), 4-methylcatechol (4-MC), and 3,4-dihydroxyphenylacetate (DOPAC), all obtained from Sigma chemical, were prepared daily using doubly distilled water. All solutions were purged with nitrogen and maintained under a blanket of nitrogen during analysis to avoid autooxidation of the catechol. 1 to 2 mM salicylic acid (Aldrich Chemical) was added to each stock solution. Salicylate fluoresces in the visible range (435 nm) when exposed to 337 nm light, which allows visualization of the focussed laser beam in the solution. Salicylate is apparently not electroactive in the potential region of interest unless it has been adsorbed unto the electrode surface (vida infra). Table 1 lists molar concentrations and ionic strengths of the buffer systems used in this study. Buffers of varying composition were chosen over a potential range in which the catechols of

interest are reasonably stable with respect to autooxidation. Monobasic sodium phosphate monohydrate and dibasic sodium phosphate heptahydrate were purchased from J. T. Baker Inc. All other chemicals were obtained from Fisher Scientific. All chemicals were reagent grade and used without further purification.

Electrodes and Apparatus. Electrodes were constructed as previously reported (21). An 11 μm carbon fiber (Amoco Performance Products, Inc.) was aspirated into a glass capillary which was pulled down around the fiber using a vertical pipet puller (Harvard Bioscience), sealed with epoxy (Epotek 301) and filled with colloidal graphite for electrical contact.

Electrochemical experiments were performed using a locally constructed low noise potentiostat in the three electrode mode. A sodium saturated calomel reference electrode (SSCE) and a platinum auxiliary electrode completed the circuit. Electrochemical reversibility was characterized by waveslope, which was calculated for each voltammogram by plotting $\log\{(i_{lim}-i)/i\}$ vs potential (E) in accord with the following expression:

$$E = E_{1/2} + \frac{2.303\ RT}{nF} \log \frac{i_{lim}-i}{i}$$

The apparatus used for laser treatment of microelectrodes is shown in Figure 1. A commercial stock pulsed nitrogen laser obtained from Laser Science Incorporated (VSL-337ND) was employed. All experiments were carried out at a laser pulse frequency of 20 Hz and each pulse had a duration of 3 ns. Electrodes were held at -0.200 volts during laser treatment which consisted of 150 to 200 pulses (7 to 10 s). The laser beam was reflected through a prism, focussed with a 150 mm focal length lens, and passed through the bottom of the electrochemical cell before striking the electrode. The electrochemical cell and all optics were constructed of fused silica. The laser spot size was approximately 100 μm. Using a 0.050 molar absorptivity for salicylate (λ=337 nm), and assuming a ten percent loss at each optical interface, a peak laser pulse power of 280 MW/cm^2 was calculated.

RESULTS AND DISCUSSION

I. Salicylate as probe for laser beam location. Salicylate fluorecses in the visible range (435 nm) after absorption of ultraviolet light(λ_{max} = 310 nm) and has been used here to locate the laser beam in solution. The nitrogen laser emits 337 nm light, which is at the base of the absorption peak of salicylate, so there is minimal absorption. Thus salicylate offers a means for beam location

with only small losses of laser power due to solution absorption. The calibration curve for the absorption of 337 nm light for several concentrations of salicylate in pH 7.4 citrate/phosphate is linear with a slope of 0.050 and an intercept of 0.020. A 2.0 mM solution of salicylate was found to have an absorbance of only 0.127. In all cases, the loss of power due to solution absorption was calculated to be less than 40%, resulting in at least 280 MW/cm^2. It has been previously reported that at least 20 MW/cm^2 is required to activate glassy carbon (18), and about 45 MW/cm^2 is required to activate the basal plane of highly ordered pyrolytic graphite (9).

Laser beam visualization with salicylate aided in locating the beam; however, alignment of the 11 μm diameter electrode into the focussed laser beam (ca 100 μm) was fine tuned by monitoring the electrode current during placement in the laser beam. Figure 2 shows a typical response when the electrode is located squarely in the laser beam. In this case, the irradiation time was about 7 seconds, or 140 pulses. Each laser pulse results in a spike of cathodic current when the applied potential is -0.200 V, and some finite minimum level seems to be maintained throughout the treatment (300 pA in this case). Following the last laser pulse the current decays back to the original background level. The current passed immediately following a laser pulse appears to have two distinct time domains: first, a rapid decay and later a slower decay. The time dependence of

this current response could prove very interesting. We have not been able to model this behavior as of yet and, hence, the current observed is used only as a tool to place the electrode in the 100 μm laser beam. It should be noted that this type of response has been obtained upon laser treatment in water in the absence of supporting electrolyte. It appears the response is originating from the electrode and\or the charging of the electrical double layer rather than from the solution.

II. Voltammetric Analysis. The effect of laser treatment on the voltammetry of DA, 4-MC, and DOPAC at a carbon fiber microelectrode is shown in Figure 3. There are three noticeable differences in the voltammograms obtained after laser treatment: 1) an improved waveslope, 2) a shift in halfwave potential to a more easily oxidized value, and 3) a surface wave at about + 0.4 V vs SSCE.

1) Reversibility. The data in Figure 3 show an increase in reversibility for all three catechols after in situ laser treatment. The effect of in situ laser treatment has been examined in several different buffer systems. The average waveslopes obtained before and after laser treatment for DA, 4-MC, and DOPAC are summarized in Figures 4, 5, and 6, respectively. Voltammograms obtained following laser treatment are reversible or near reversible for DA in all buffer systems examined. This is consistent with literature reports of well behaved voltammetry for cationic DA at carbon electrodes (22,23). The variability in the waveslopes

(standard error between measurements) is decreased after laser treatment. Thus, a more consistent voltammetric response is obtained following laser treatment at these electrodes. Waveslopes for voltammograms obtained before laser treatment generally exhibit less reversible behavior with decreasing pH. This is especially evident in the citrate-containing buffer systems, consistent with data presented by Deakin et al for cations at glassy carbon electrodes (6). This dependence of voltammetric waveslopes on pH is much less evident following laser treatment and this is consistent with data concerning the effect of heat treatment on voltammetry at glassy carbon electrodes (6).

Figure 5 summarizes the waveslope data for voltammetry of 4-MC following laser treatment in several buffer systems. Again, nearly reversible behavior is seen for each case after laser treatment and the variance of the waveslope is significantly decreased in most buffer systems. The waveslope after laser treatment appears to increase with decreasing pH in the phosphate buffers, and a large voltammetric waveslope is observed for all the analytes in the citrate-containing buffers before laser treatment. In all buffers, the waveslope obtained following laser treatment was more Nernstian.

Figure 6 summarizes waveslope data for voltammetry of DOPAC following laser treatment. Voltammetric waveslopes are more reversible in every buffer system following laser treatment. However, these waveslopes are generally larger

than those observed for DA or 4-MC after laser treatment. Apparently, the oxidation of DOPAC is kinetically hindered relative to DA and 4-MC, even at laser treated electrodes. A distinct trend of increasing waveslope with pH is observed for the oxidation of DOPAC in the citrate/phosphate buffers. This is again consistent with studies on glassy carbon (6). Another interesting point is the large average variance in waveslope for the untreated electrodes, which is apparently caused by the poorly defined, irreproducible surface of the carbon fiber electrode. If this is correct, the effect of the laser treatment is to clean the electrode surface, resulting in reduction of the variation in waveslope. Laser treatment provides a more reproducible surface which also exhibits more reversible voltammetry in the buffer systems examined.

2) Halfwave Potentials. A shift in halfwave potential to more easily oxidized potentials is often apparent following laser treatment. The halfwave potentials obtained after laser treatment are also more consistent, owing to the reproducible carbon surface. The slopes of the $E_{1/2}$ vs pH plots obtained show slightly higher values than the 59.1 mV slopes that are expected. Before laser treatment the slopes obtained were 71.4, 61.5 and 71.4 mV per pH unit for DA, 4-MC and DOPAC, respectively. After laser activation these values were 65.8, 68.4 and 72.0 mV per pH unit. One explanation for the larger slope of these plots involves surface effects that are pH dependent. Adsorption of

catechol onto the electrode surface or onto a surface-bound layer might be favored at elevated pH. A linear, or near linear dependence of halfwave potential on pH is still preserved by this mechanism.

3) Surface Waves. The third noticeable difference in voltammetry after laser activation shown in Figure 3 is the surface wave at approximately +0.4 V vs SSCE. This wave appears to be a result of adsorption of salicylate, which is placed into the working solution to aid in beam location. Laser activation for dopamine in the absence of supporting electrolyte and salicylate did not result in this surface wave (n=3), whereas laser activation of these electrodes following the addition of salicylate to the solution resulted in voltammetry with the surface wave present (n=3). Prewaves, presumably due to analyte adsorption were observed for voltammetry in pH 2.7 and 4.1 citrate/phosphate buffers, as well as occasionally in the pH 4.3 phthalate buffer system. These surface waves were observed in 87% of the experiments with DA (n=35) in these buffers and 40% of the experiments involving DOPAC (n=30). These waves were rarely observed before laser treatment, were fairly sharp peaks immediately following laser treatment, and were rarely present on subsequent scans. Also, there was no cathodic peak noticed on the return scan, leading one to believe the wave was due to oxidation of surface-bound species that were subsequently desorbed from the surface. It should be noted that voltammograms displaying this prewave generally do not

display a surface wave at +0.4 V. This phenomenon was not studied further since the surface waves were not in the potential range of the $E_{1/2}$ of the species of interest.

III. Voltammetry in Citrate Buffers. The largest effect of buffer composition on voltammetry was observed with the buffer system that contained citrate. Citrate containing buffers have been known to show anomalous effects on voltammetry at carbon electrodes (6,19,24). One explanation for this would be a high affinity for citrate adsorption onto the carbon fiber. For this reason laser activation was attempted in a citrate buffer, pH 6.0. The resultant voltammograms for DA and DOPAC are shown in Figures 7 and 8, respectively. Voltammograms of DA are somewhat peak-shaped after laser treatment in citrate buffer, whereas voltammograms of DOPAC are not. Additionally, peak-shaped voltammetry is observed only on the immediate scans after laser treatment. Several voltammetric scans will result in totally sigmoidal voltammetry (Figure 7C). It appears that DA strongly adsorbs to the laser treated electrode surface, while DOPAC does not in citrate buffer. Based on this assumption there are at least two possible, and highly speculative explanations for this phenomenon. First, it is possible that citrate has a high affinity for adsorption onto the laser cleaned carbon surface. Adsorbed citrate, triply anionic at pH 6, could lead to an ion exchange mechanism for cations at the surface. In this situation a Donnan exclusion would reduce

partitioning of anionic analytes into the citrate "layer". A second explanation could be an enhancement of the natural affinity of carbon for cations preferentially over anions. Selectivity of carbon fibers for cations has been documented previously (22,23). This phenomenon, which might stem from the formation of surface oxides (4), could be magnified at surfaces cleaned, or activated, in the presence of citrate. The entire explanation is most likely a combination of these and perhaps other factors. It is conceivable that the freshly exposed, laser treated carbon will adsorb solution species, including the electroactive species, resulting in altered voltammetric properties.

The data presented in this paper appear to be consistent with a mechanism where in situ laser treatment leads to ablation of the carbon surface, which results in a more roughened, pure carbon surface. Clearly, this treatment of the surface improves charge transfer kinetics, and, in some cases increases adsorption. The electrode surface might adsorb solution species, including the analyte, on the freshly exposed carbon. The occurrence of analyte adsorption following laser treatment appears to further improve the charge transfer kinetics at microelectrodes, and in extreme cases, results in peak shaped voltammograms. This adsorption appears to be medium dependent, and the presence of citrate is clearly special. This effect is not observed in phosphate alone, and the citrate interaction with the carbon fiber deserves further

study. As with almost all activation procedures, laser treatment is a short-lived activation scheme. However, an electrode can be easily reactivated once the system is aligned properly. It is evident that laser treatment greatly improves the voltammetric response of carbon fiber microdisk electrodes for the three catechols considered and is a simple, fairly inexpensive method for obtaining consistent, well-behaved voltammetry at carbon microdisk electrodes.

CREDIT

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Table I. List of buffer systems employed during this study.

BUFFER SYSTEM	CONCENTRATION (M)	IONIC STRENGTH (M)
A. pH 6.0 Phosphate	0.1002	0.117
B. pH 7.4 Phosphate	0.100	0.241
C. pH 8.0 Phosphate	0.050	0.569
D. pH 2.7		
Citrate	0.0858	0.0512
Phosphate	0.0284	
E. pH 4.1		
Citrate	0.0671	0.158
Phosphate	0.0769	
F. pH 7.4		
Citrate	0.0091	0.888
Phosphate	0.181	
G. pH 4.3 Phthalate	0.050	0.056
H. pH 6.0 Citrate	0.200	0.744

FIGURE LEGENDS

Figure 1: Schematic of laser activation apparatus. A-laser, B-reflecting prism, C-focusing lens, D-electrochemical cell, E-carbon microdisk electrode, F-Faradaic cage.

Figure 2: Photograph of an oscilloscope screen showing the response from potentiostat output during laser treatment for a squarely hit electrode. Y-axis: 100 pA/div. X-axis: 2 s/div. Electrode potential: -0.200 V vs SSCE. The time constant of the potentiostat is 5×10^{-4} s.

Figure 3: Voltammetry in pH 7.4 citrate/phosphate buffer before (solid lines) and after (dotted lines) laser activation for dopamine (DA), 4-methyl catechol (4-MC), and 3,4-dihydroxphenylacetate (DOPAC). Scan rate: 100 mV/s. Analyte concentrations are 1×10^{-4} M. Activation time was approximately 10 s.

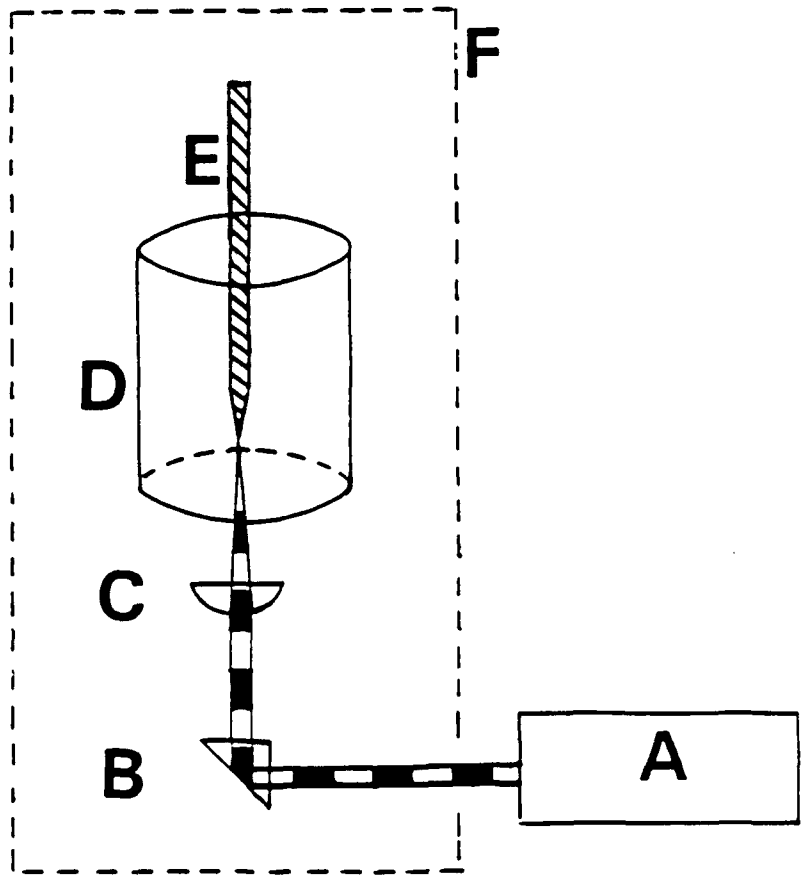
Figure 4: Average waveslopes for voltammetry of DA at a disk shaped carbon fiber microelectrode before (open boxes) and after (shaded boxes) laser activation. Error values (box widths) shown are standard error of the mean. A,B and C are phosphate buffers pH 6.0, 7.4 and 8.0, respectively. D,E and F are citrate/phosphate buffers pH 2.7, 4.1 and 7.4, respectively. G is a phthalate buffer pH 4.3.

Figure 5: Average waveslopes for voltammetry of 4-MC at a disk shaped carbon fiber microelectrode before (open boxes) and after (shaded boxes) laser activation. Error values (box widths) are standard error of the mean. A,B and C are phosphate buffers pH 6.0, 7.4 and 8.0, respectively. D,E and F are citrate/phosphate buffers pH 2.7, 4.1 and 7.4, respectively. G is a phthalate buffer pH 4.3.

Figure 6: Average waveslopes for voltammetry of DOPAC at a disk shaped carbon fiber microelectrode before (open boxes) and after (shaded boxes) laser activation. Error values (box widths) are standard error of the mean. A,B and C are phosphate buffers pH 6.0, 7.4 and 8.0, respectively. D,E and F are citrate/phosphate buffers pH 2.7, 4.1 and 7.4, respectively. G is a phthalate buffer pH 4.3.

Figure 7: Voltammetry of 1×10^{-4} M DA in pH 6.0 citrate buffer. Scan A is at a freshly cut electrode, B is immediately after a 10 s laser treatment at 20 Hz, and C is the response after four voltammograms had been taken.

Figure 8: Voltammetry of 1×10^{-4} M DOPAC in pH 6.0 citrate buffer. Scan A is at a freshly cut electrode, B is immediately after a 10 s of laser treatment at 20 Hz, and C is the next scan after B.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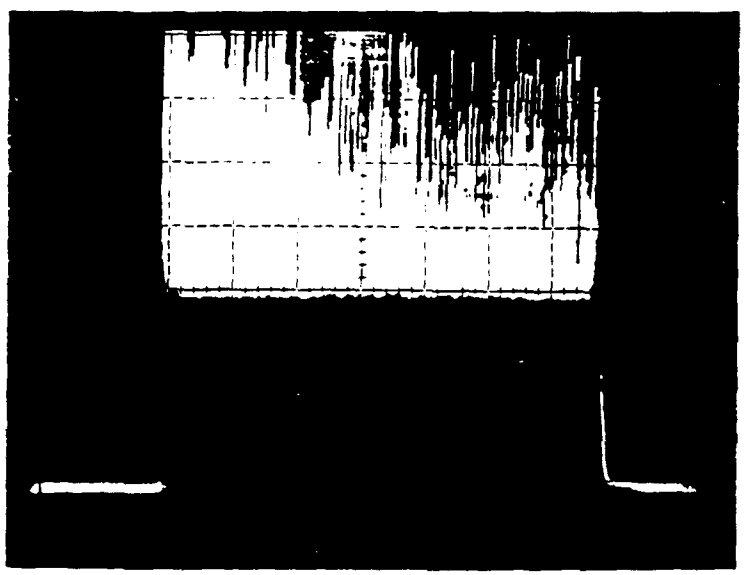

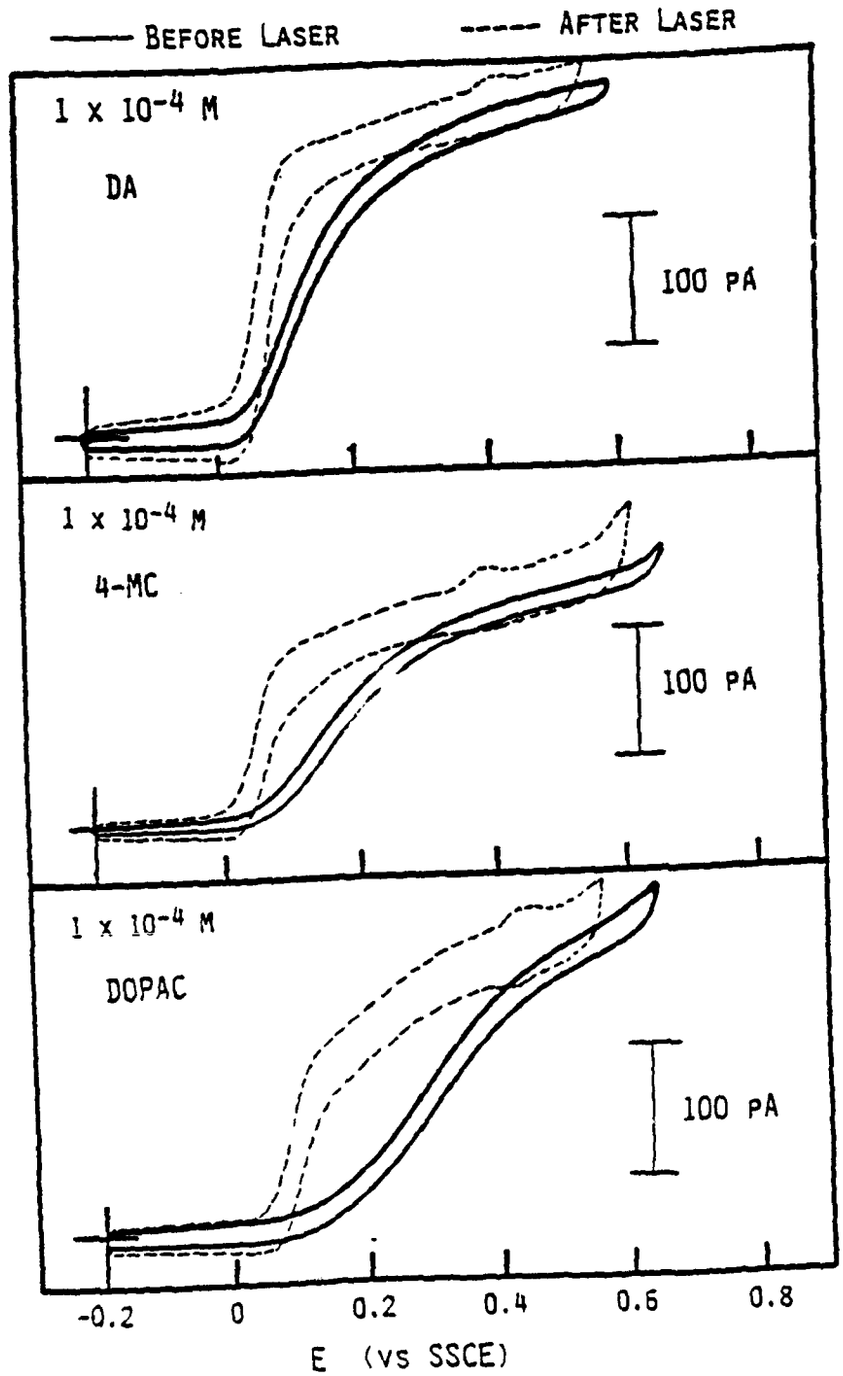
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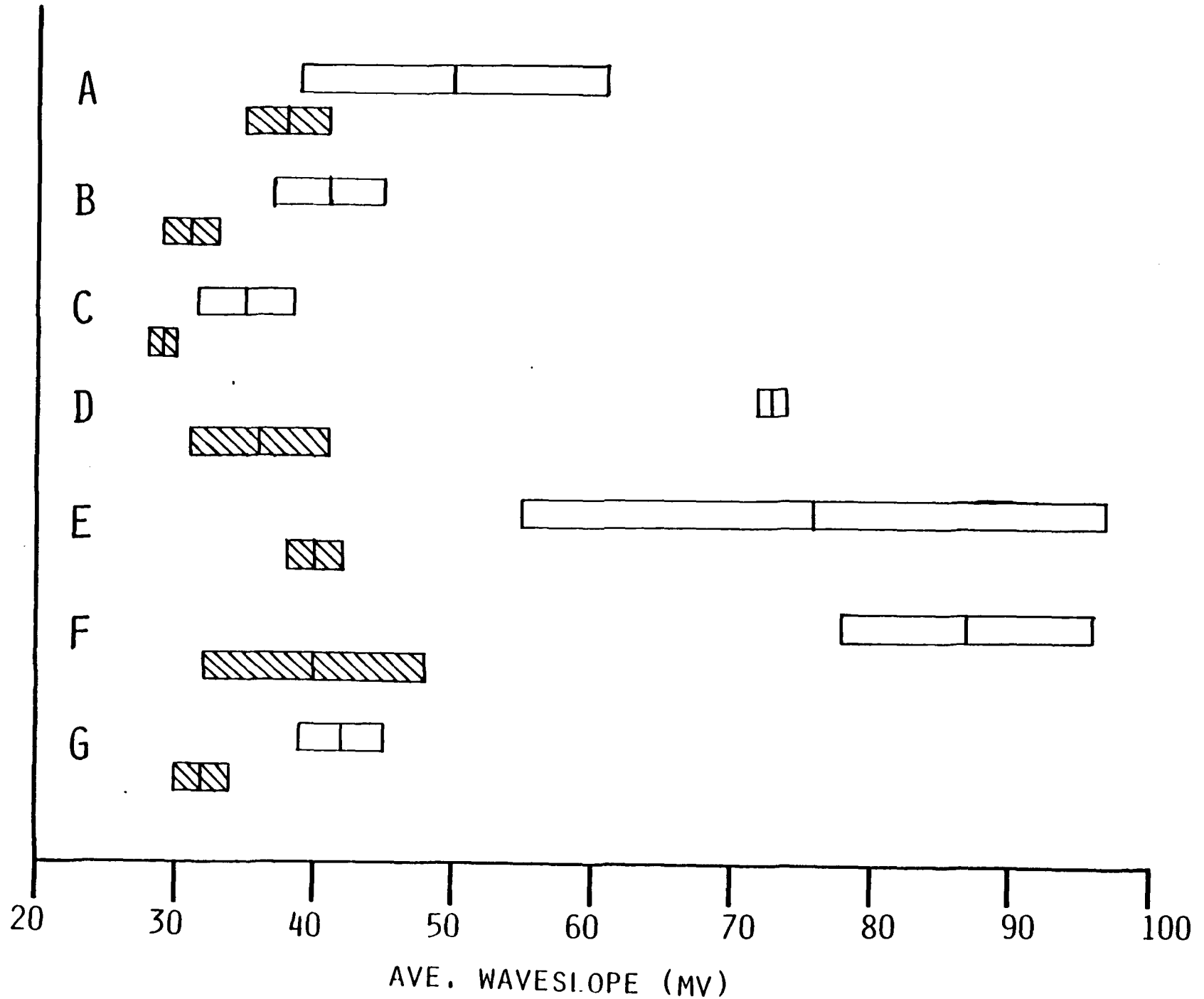
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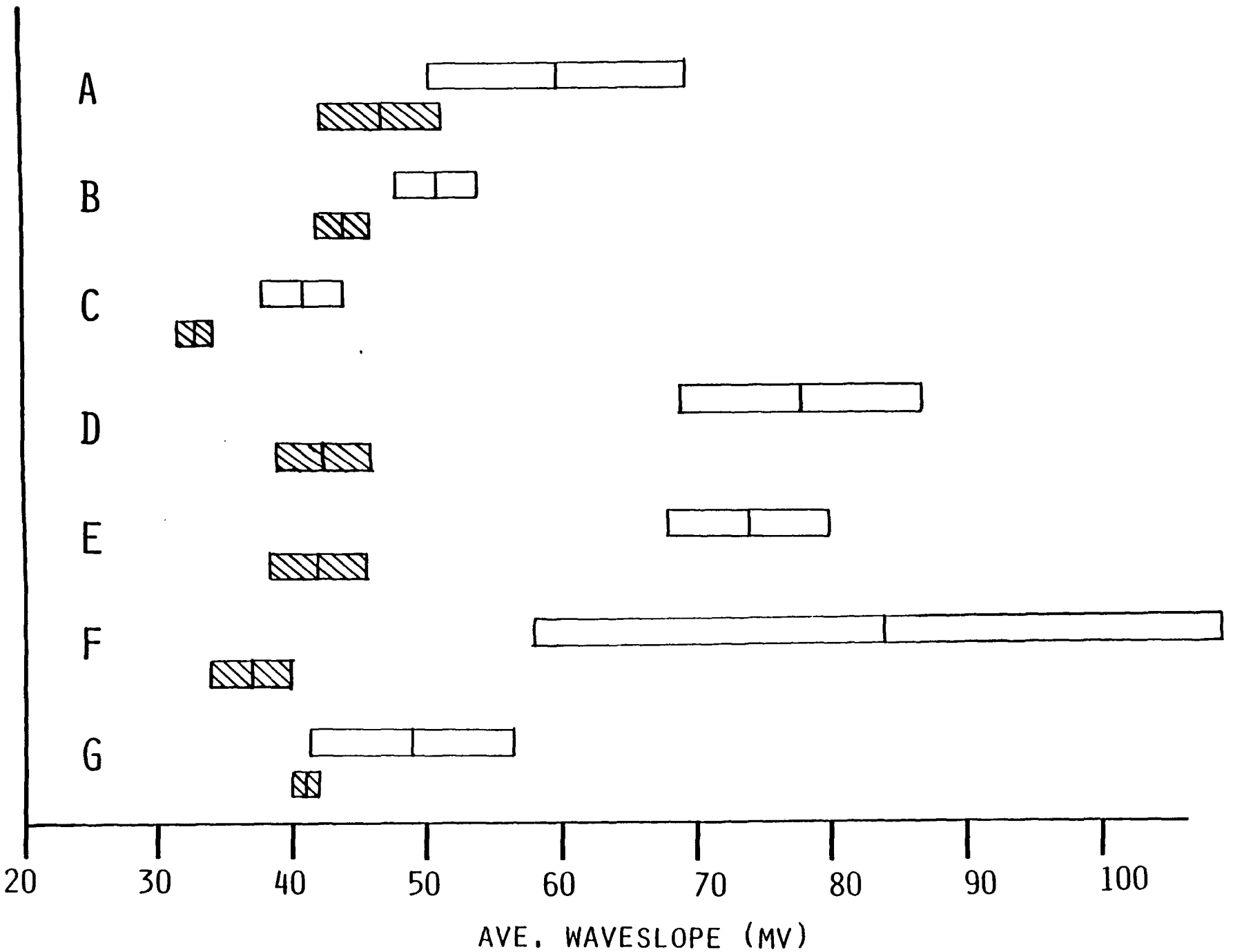
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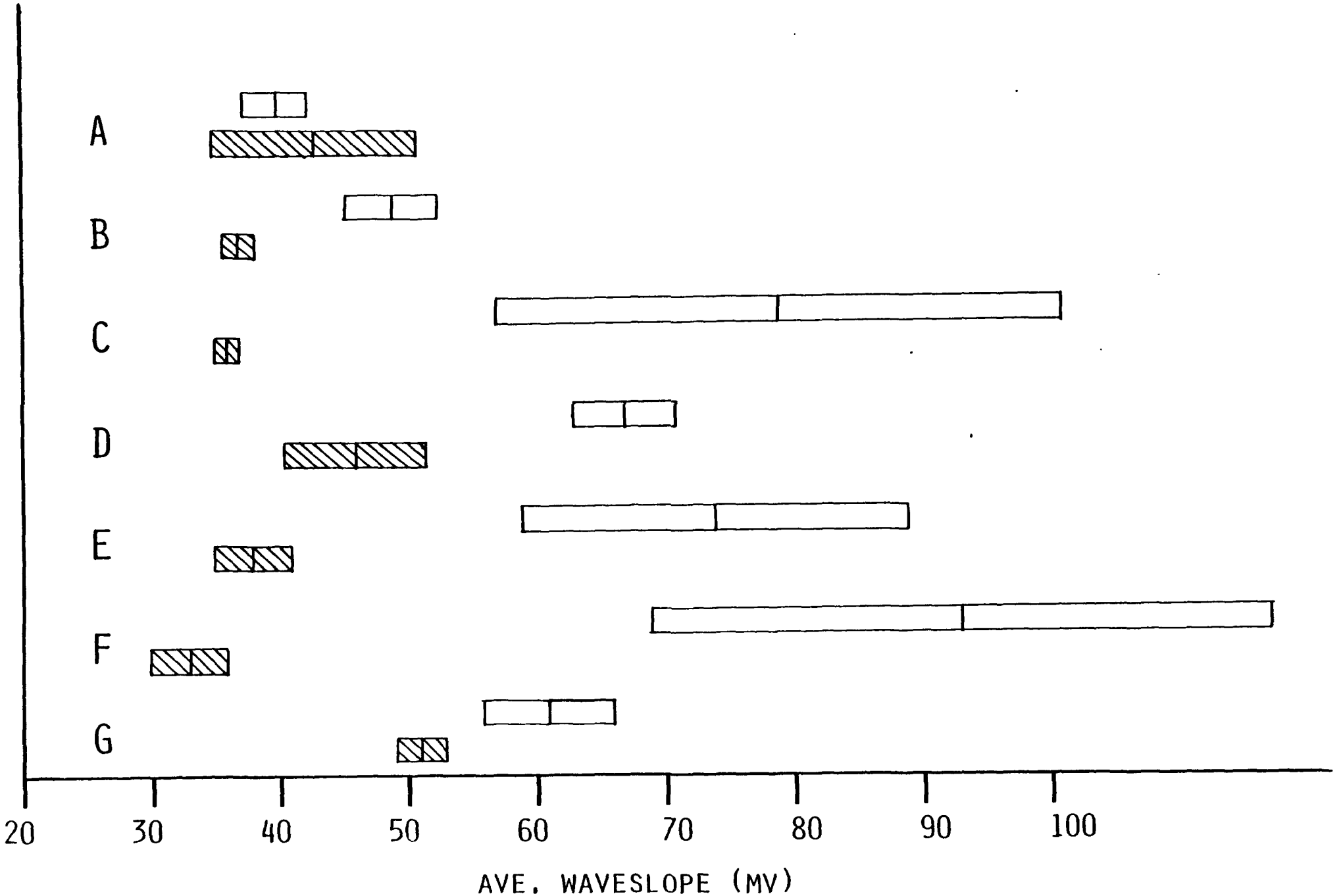
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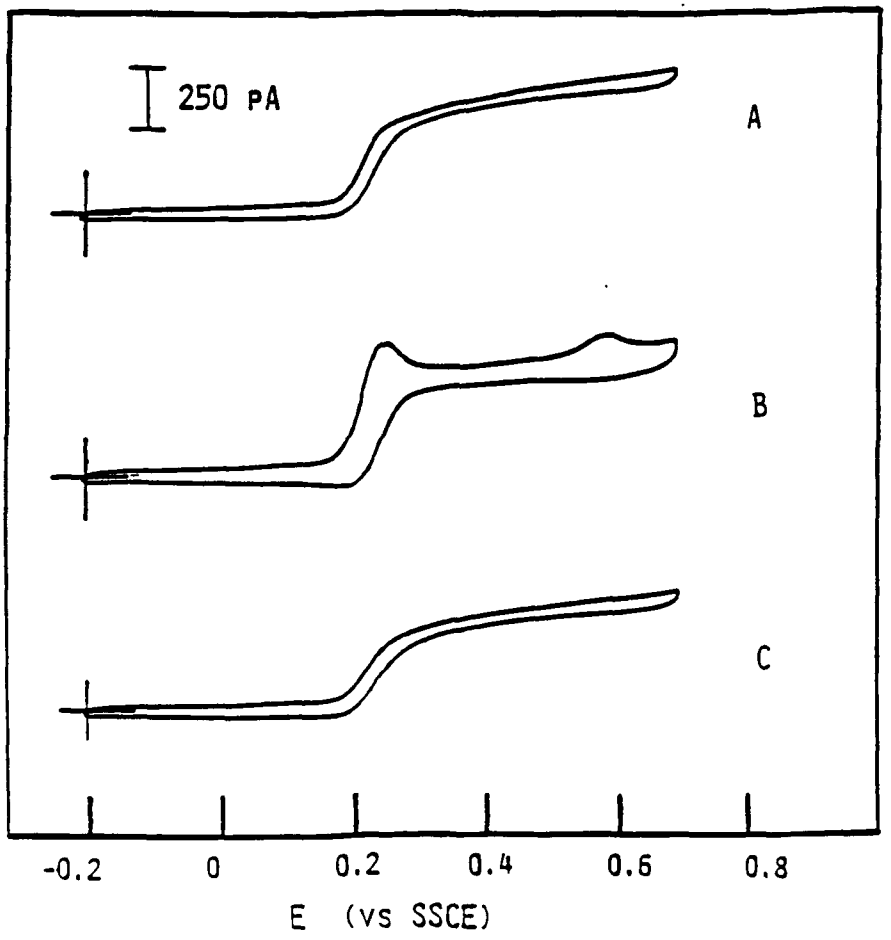
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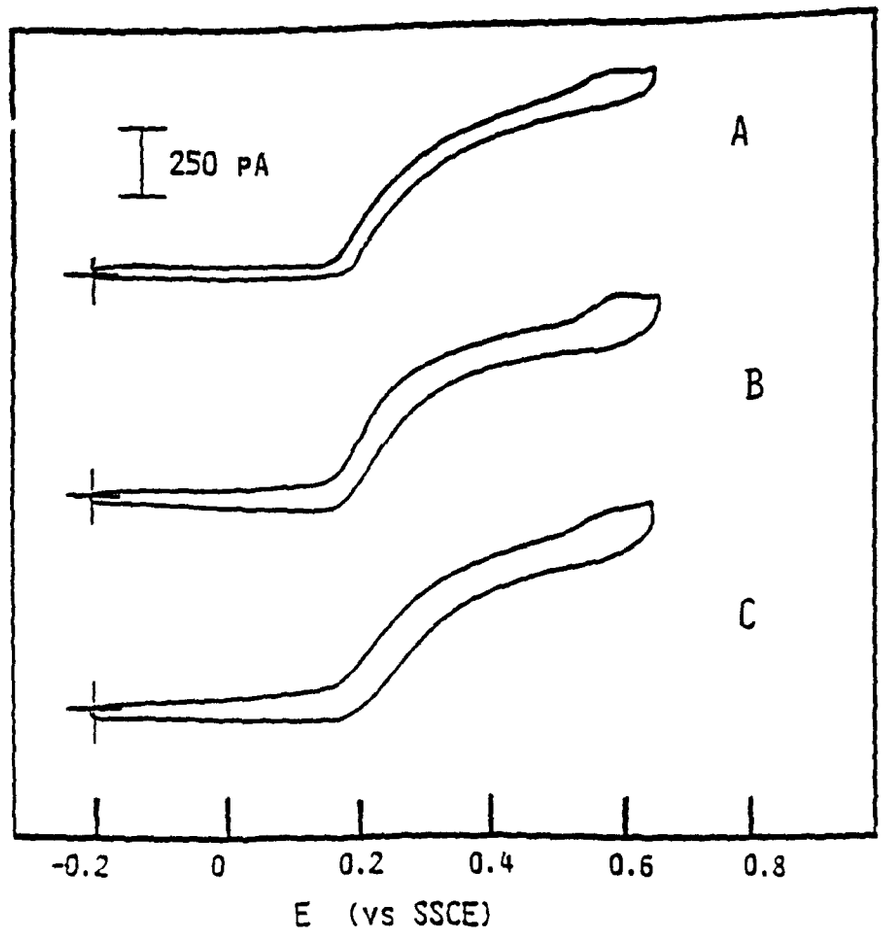
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